

L123.015



## PATENT SPECIFICATION

NO DRAWINGS

L123.015

Date of Application and filing Complete Specification: 4 Aug., 1965.

No. 33276/65.

Application made in United States of America (No. 388,268) on 7 Aug., 1964.

Complete Specification Published: 7 Aug., 1968.

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Index at acceptance:—C7 D(8H, 8U, 8W, 8Y, 8Z5, A1); H1 M(3B2D, 3B3H, 3B3J, 3B3X)

Int. Cl.:—B 22 f 1/00

## COMPLETE SPECIFICATION

## A process for producing Sintered Anodes

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignee of HARRY WALKER HOLLAND and WALTER FRED HELVEY) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for making anodes for electrolytic capacitors and the capacitors made therefrom.

Electrolytic capacitors of the type having a porous plug as the anode are made by molding particles of a suitable metal, such as tantalum or columbium for example, into a desired shape and sintering that body to produce a porous metal anode. By means of an electrolytic process, the surface of the sintered particles forming the plug are converted into an oxide layer. This oxide layer forms a dielectric between the tantalum anode, for oxide layer forms a dielectric between the tantalum anode, for example, and a subsequently applied conductive cathode layer. The oxidized porous metal anode is then dipped into a concentrated manganese nitrate solution and thereupon heated in an oven to convert the manganese nitrate to manganese oxide. This step may be repeated several times to provide for a complete filling of the pores of the anode with manganese oxide. The plug is then subjected to a "healing" operation, as by electrolytically reoxidizing the anode. By means of this process, manganese oxide in and around any defects in the anode oxide layer is converted to other more insulating forms of manganese oxide. This converted manganese oxide helps reduce direct current leakage while the remainder of the manganese oxide acts as the dry electrolyte for the capacitor. A conductive layer of graphite is then applied to the anode, whereupon the anode can be placed in a cathode can with the carbon layer conducting

to the can. The capacitor is completed by attaching anode and cathode leads and sealing the assembly.

This invention applies to capacitors made by the above process as well as to capacitors made by other processes, providing that a metal powder of the type indicated hereinbelow is pressed into a shape and sintered to form the anode.

The invention is based on the discovery that the quality of the metal powder used in the manufacture of such anodes has a direct bearing on the quality of the sintered anode, as measured by the performance characteristics of the finished capacitor employing that anode. In particular, it has been found that capacitors having anodes made with metal powders containing excessive amounts of carbon or oxygen impurities have lower breakdown voltages and higher leakage currents. Although these two impurities will react at the high sintering temperatures and form carbon monoxide, which is removed by the vacuum pumps during the heating operation, it has been found beneficial to use powder having a specific range of carbon and oxygen impurities and to add reactant material for the purpose of lowering the impurity levels to certain optimum carbon and oxygen contents in the finished anode, whereby superior capacitors are produced.

According to the present invention, a process for producing an anode for an electrolytic capacitor comprises providing a powder of an anode metal selected from the group consisting of tantalum, columbium, tungsten, hafnium, titanium, and zirconium, said metal powder containing less than 500 ppm carbon and less than 5000 ppm oxygen, mixing with said powder an amount of carbon-containing material providing sufficient carbon, together with the carbon in the powder, to react with and remove as carbon monoxide during heating that portion of the contained oxygen in said powder above an oxygen level of 1500 ppm, pressing said powder mixture into an anode

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- shape and sintering said shape under vacuum conditions to produce a sintered anode having an oxygen content of from 1000 to 1500 ppm and less than 30 ppm carbon.
- 5 It has been found that superior capacitors are produced when the oxygen and carbon contents of the metal powder are between 1200 and 5000 ppm oxygen and less than 500 ppm carbon, and where tantalum carbide or graphite
- 10 is added to this powder to form carbon monoxide during sintering but leaving as residuals in the finished tantalum anode an oxygen content of from 1000 to 1500 ppm and less than 30 ppm carbon.
- 15 The carbon containing material may consist of graphite or a carbide of at least one of the anode metals, or a mixture of graphite and a carbide of at least one of the anode metals.
- 20 The amount of carbon containing material added to the anode metal powder is determined on the basis of the stoichiometric amount of carbon needed to react with the contained oxygen during the sintering process. A convenient manner of calculating the amount of metal carbide required is given below in regard to a tantalum metal powder having certain oxygen and carbon contents.
- 25 A tantalum metal powder prepared from tantalum roundels is found to have a carbon content of about 90 ppm (parts per million) and an oxygen content of 2400 ppm. The desired final carbon content is less than 30 ppm and the desired final oxygen content of the sintered anode is about 1300 ppm, which is in the desired range of 1000 to 1500 ppm oxygen. Assuming that all of the original 90 ppm carbon will be reacted during sintering to form carbon monoxide, it is assumed that
- 30 16
- 40  $90 \times \frac{12}{12} = 90$  ppm of oxygen will be removed,
- 45 equal to 120 ppm of oxygen. Since 1300 ppm of residual oxygen is desired, this leaves 2400 minus (120 + 1300), equal to 980 ppm of

oxygen to be removed from the powder by some amount of carbide. Using tantalum carbide with a molecular weight of 193, the amount of tantalum carbide needed to react with 980 ppm of oxygen can be determined as follows using equivalent weights:

$$\frac{980 \text{ ppm O}_2}{16} = \frac{\text{ppm TaC}}{193}$$

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The amount of tantalum carbide required thus will be about 11,711 ppm TaC. As a percentage addition to the tantalum powder, the amount of TaC to be added would be 11,711 divided by one million, equal to 1.17%.

An amount of 1.17 per cent TaC was added to a tantalum powder sample having the original carbon and oxygen contents indicated above. This mixture was molded into anode shapes and sintered at a temperature above 1800°C. and under a vacuum of below  $10^{-4}$  mm of mercury. Carbon and oxygen combined to form carbon monoxide which was drawn off by the vacuum pumps. The sintered anode plug was found on chemical analysis to have a residual carbon content of about 20 ppm and a residual oxygen content of about 1400 ppm, which is within the desired range. The deviation from the predicted oxygen content of 1300 ppm was due to the approximations and assumptions made, as well as an expected error of  $\pm 100$  ppm in oxygen analysis. The method outlined above for determining the amount of carbide needed to reach a given desired final oxygen content is satisfactory for most purposes.

Several other samples of the same basic tantalum powder were mixed with varying amounts of tantalum carbide, pressed into anode shapes and sintered under the same conditions outlined above. Table I shows the treatment performed on each sample as well as the oxygen and carbon analysis of the sintered plug.

TABLE I

## Chemical Analysis

Lot No.	Treatment	Parts Per Million	
		C	O <sub>2</sub>
—	Original Ta Powder	90	2400
1	None, 100% original powder	10	1900
2	1% TaC added	20	1400
3	1.17% TaC added	20	1400
4	1.30% TaC added	20	1100
5	1.43% TaC added	20	1200

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Table II shows the electrical performance characteristics of capacitors made with these anodes.

TABLE II  
Performance—22  $\mu$ f, 50 Volt Capacitors

Lot No.	Breakdown Voltage, Volts	Capacitance C, $\mu$ f	Leakage Current I, $\mu$ A	Dissipation Factor, %
1*	245	—	—	—
2	280	21.9	.175	3.38
3	293	21.3	.317	2.98
4	320	22.0	.14	3.4
5	267	22.0	.031	3.33

\* All lost in reformation.

Another series of tests were conducted using 5 a tantalum powder having an original carbon content of 100 ppm and an oxygen content of 2300 ppm. Various amounts of tantalum carbide were added to this powder and sintered anode plugs were prepared from the mixture as above. Table III shows the chemical analysis of the plugs as well as the performance characteristics of 33  $\mu$ f, 35 V capacitors made with these plugs. Tantalum carbide was not added to Lot No. 6. 10

TABLE III

Lot No.	Analysis, C	PPM O <sub>2</sub>	Breakdown Voltage, V	Capacitance $\mu$ f	Leakage Current $\mu$ A	Dissipation Factor, %
6	20	2000	252	33.2	.138	2.86
7	20	1800	259	34.0	.057	3.36
8	20	1200	282	35.37	.065	3.44
9*	80	800	173	—	—	—

\* All lost in reformation at 40 volts.

As seen above the capacitors made using the anodes having carbon and oxygen contents after sintering of less than 30 ppm carbon and from 20 1000 to 1500 ppm oxygen performed particularly well. The capacitors made from plugs with analysis outside this range had lower breakdown voltages and higher leakage currents and did not show as great a yield.

It is to be noted that when the oxygen content of the tantalum powder is too low or the carbon content too high, then oxides of tantalum, e.g., can be added to the powder before sintering to bring the final oxygen content of the sintered plugs into the indicated 25 range. The amount of oxides added would be sufficient to raise the oxygen content of the

powder above its original content, but less than the maximum of 5000 ppm.

Although the process of this invention has been described hereinabove with reference to tantalum as the anode material, the process can also be used in regard to the preparation of sintered anodes of metals other than tantalum, namely, columbium, tungsten, hafnium, titanium, and zirconium. These metals are all capable of forming the dielectric oxide films needed for capacitor usage. In the preparation of the powders of these metals, the carbide added as the reactive material could be the carbide of the particular metal being used for the anode or it could be the carbide of one of the other anode metals. 35 40 45

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**WHAT WE CLAIM IS:—**

1. A process for producing an anode for an electrolytic capacitor which comprises providing a powder of an anode metal which is tantalum, columbium, tungsten, hafnium, titanium, or zirconium, the powder containing less than 500 ppm carbon and less than 5000 ppm oxygen, mixing with the powder an amount of carbon-containing material providing sufficient carbon, together with the carbon in the powder, to react with and remove as carbon monoxide during heating that portion of the contained oxygen in the powder above an oxygen level of 1500 ppm, pressing the powder mixture into an anode shape and sintering the shape under vacuum conditions to produce a sintered anode having an oxygen content of from 1000 to 1500 ppm and less than 30 ppm carbon. 30
5. A process as claimed in claim 4, in which the anode shape is sintered at a temperature above 1800°C. and at a vacuum of below 10<sup>-4</sup> mm. of mercury. 35
10. A process as claimed in claim 1, in which the metal powder contains considerably less than 5000 ppm oxygen and an oxide of at least one of the anode metals is added to the metal powder to raise the contained oxygen level to a point above the original amount but still below 5000 ppm. 40
15. A process for producing an anode for an electrolytic capacitor as claimed in claim 1, substantially as hereinbefore particularly described. 45
20. An anode for an electrolytic capacitor, whenever produced by the process claimed in any of claims 1 to 7. 50
25. A process as claimed in claim 1 or 2 in which the carbon-containing material consists of graphite or a carbide of at least one of the anode metals, or a mixture of graphite and a carbide of at least one of the anode metals.
20. 2. A process as claimed in Claim 1, in which the metal powder contains between 1200 and 5000 ppm oxygen.
3. A process as claimed in claim 1 or 2 in which the carbon-containing material consists of graphite or a carbide of at least one of the anode metals, or a mixture of graphite and a carbide of at least one of the anode metals.
4. A process as claimed in claim 1 or 2, in which the metal powder consists of tantalum and the carbon-containing material is composed of tantalum carbide.
5. A process as claimed in claim 4, in which the anode shape is sintered at a temperature above 1800°C. and at a vacuum of below 10<sup>-4</sup> mm. of mercury.
6. A process as claimed in claim 1, in which the metal powder contains considerably less than 5000 ppm oxygen and an oxide of at least one of the anode metals is added to the metal powder to raise the contained oxygen level to a point above the original amount but still below 5000 ppm.
7. A process for producing an anode for an electrolytic capacitor as claimed in claim 1, substantially as hereinbefore particularly described.
8. An anode for an electrolytic capacitor, whenever produced by the process claimed in any of claims 1 to 7.
9. An electrolytic capacitor comprising an anode produced by the process claimed in any of claims 1 to 7.

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Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.  
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which  
copies may be obtained.

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